THE DIFFERENCE IN CHEMICAL ACTIVITY OF FREE AND SEMICOMBINED WATER AS ILLUSTRATED BY THE EFFECT OF NEUTRAL SALTS ON HYDROLYSIS OF ACETIC ANHYDRIDE

DISSERTATION

Submitted to the Board of University Studies of The Johns Hopkins University in Conformity with the Requirements for the Degree of Doctor of Philosophy

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by
GERALD CHARLES CONNOLLY.
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THE DIFFFRENCE IN CHEMICAL ACTIVITY OF FREE AND SEMICOMBINED WATER AS ILLUSTRATED BY THE EFFECT OF NEUTRAL SALTS ON HYDROLYSIS OF ACETIC ANHYDRIDE

The present investigation was undertaken for the purpose of obtaining further evidence on the solvate theory of solution. The solvate theory was proposed in this laboratory by Professor Harry C. Jones in 1900, to account for certain apparently abnormal freezing-point lowerings produced by certain electrolytes when dissolved in water. From this beginning the work has expanded in many directions until there are at present sixteen distinct lines of evidence, all pointing to the validity of the view that when a salt is dissolved in a solvent there is more or less combination between the salt, or the ions resulting from it, and the solvent. The magnitude of this solvation depends upon the nature of both the solvent and the dissolved substance.

HYDROLYSIS.

The term hydrolysis is applied to a number of chemical reactions in which there is first the addition of water to a complex, and then the decomposition of the product into simpler substances. From this definition it is evident that the reactions included under hydrolysis are numerous and varied.

There are in general four main divisions of hydrolysis:

(1). Hydrolysis of metallic salts.

(2). Hydrolysis of esters and closely associated substances, such as amides, nitriles, acid chlorides, acid anhydrides, etc.

(3). Hydrolysis of complex carbohydrates and glucosides.

(4). Hydrolysis of polypeptides and proteins.

In this discussion we will confine ourselves almost entirely to the first two divisions, for these are the only forms of hydrolysis which come within the scope of this investigation.

HYDROLYSIS OF ACETIC ANHYDRIDE.

The hydrolysis of acetic anhydride has been studied by several investigators with varying degrees of success. The term "hydrolysis of acetic anhydride" is used here in preference to the term "hydration of acetic anhydride" used by other investigators, since it is more in accordance with the definition of hydrolysis previously stated.

Menschutkin and Vasilieff,[1] in studying the decomposition of acetic anhydride by water, attempted to find a constant for the velocity of hydrolysis. They did not succeed because the two substances were not miscible in all proportions, and no solvent could be found that did not act either on the substances themselves or on the products of the reaction. They studied the change in a homonogeneous mixture of acetic acid, acetic anhydride and water, and found that the reaction was not as rapid as had generally been supposed. With a mixture of equal portions of acetic anhydride and water at 19° only about one-half the anhydride was hydrolyzed at the end of six hours, and eleven days were necessary for complete hydrolysis. In the following table a comparison is made

1 Journ. Russ. Phys. Chem. Soc., **21**, 188 (1889).

between the velocities of decomposition of acetic anhydride, acetamide and ethyl acetate by one gram-equivalent of water at 100° under the same conditions. The experiments were carried out in the presence of acetic acid.

Substance	Acet. Anhyd. + 1 H_2O	Acetamide + 1 H_2O	Ethyl Acetate + 1 H_2O
Acetic Acid Added	11.86%	15.85%	11.45%
Time	Decomposition in per cent.		
1 min.	25.68	4.51	0.2
11 min.	83.9	4.64	0.5
61 min.	98.5	4.94	0.87
121 min.	99.5	5.82	0.99
181 min.	99.7	6.41	...

The acetic anhydride was almost entirely decomposed at the end of one hour, while the decomposition of the acetamide was slight and that of the ethyl acetate had hardly begun.

Hinsberg[2] showed that acetic anhydride is soluble in water in the anhydride state, and that the presence of water is not an obstacle to the employment of the anhydride as such.

A. and L. Lumiere and Barbier[3] found that a solution of acetic anhydride in water possesses practically all the properties of acetic anhydride and is sufficiently stable for acetylation purposes. By simply shaking the anhydride with water, they obtained a twelve per cent. solution, which readily acetylated amino- and imino-compounds.

2 Ber. d. deutsch. chem. Gesell., **23,** 2962 (1890).
3 Bull. Soc. Chim. (III) **33,** 783 (1905).

In the second paper[4] A. and L. Lumiere and Barbier showed that if more than twelve parts of the anhydride are used, solution is incomplete. They prepared five and ten per cent. solutions of acetic anhydride in cold water and set them aside. From these solutions aliquot parts were withdrawn every ten minutes and added to a slight excess of aniline, the excess being known. Reaction took place quantitatively between the aniline and the acetic anhydride not hydrolyzed by the water, with the formation of acetanilide and an equivalent of acetic acid. The total acid present was then determined by titration with a normal solution of sodium hydroxide in the presence of phenolphthalein. From this the degree of hydrolysis of the acetic anhydride was calculated, and the results obtained are given in the table below.

From these results it can be seen that the rate of hydrolysis is fairly rapid at first and then gradually decreases. It is the more rapid the greater the initial dilution of the anhydride and the higher the temperature.

Alcoholic solutions of the anhydride were also prepared, and it was found that when molecular proportions were used, esterification was incomplete, even after a month.

HYDROLYSIS OF ACETIC ANHYDRIDE BY WATER.

	5% Solution		10% Solution	
Time	15°	0°	15°	0°
0	9.2	4.6	11.5	9.8
10	52.5	35.0	58.2	34.6
20	74.2	48.4	71.0	51.1
30	89.7	60.8	78.9	60.0
40	95.7	69.0	86.6	67.0
50	100.0	76.2	91.7	73.3
60	....	80.4	93.3	77.9
70	....	85.5	94.6	81.5
80	....	89.6	96.4	85.1
90	....	93.8	97.9	88.9
100	....	96.9	100.0	92.8
110	....	100.0	....	94.8
120	....	....	....	95.8
140	....	....	....	98.5
160	....	....	....	100.0

4 Bull. Soc. Chim. (III) **35**, 625 (1906).

Benrath,[5] by means of change in density, attempted to measure the rate at which acetic anhydride combines with water, using acetic acid as the solvent. He concluded that, with equivalent quantities of anhydride and water, the reaction was monomolecular, i. e., it depended on the concentration of only one of the reacting substances.

Rivett and Sidgwick,[6] using dilute aqueous solutions, followed the hydrolysis by determining the electrical conductivity at 25°. The velocity of hydrolysis showed that the reaction was monomolecular and was not catalyzed by hydrogen ions; and that beyond a certain point the constant decreased steadily with increasing concentration. From this they concluded that the mechanism of the hydrolysis of acetic anhydride is quite different from that of the hydrolysis of esters and amides, in which case the velocity constant is proportional to the concentration of the hydrogen ions.

Orton and M. Jones,[7] on the other hand, consider the hydrolysis of acetic anhydride to be entirely analogous to the hydrolysis of esters and amides. They conclude that the hydrolysis of acetic anhydride in acetic acid as the solvent is a slow reaction of the second order; that on dilution the increase in velocity is approximately proportional to the amount of water present, and that the relation of the velocity factor to the temperature is normal. The effect of catalysts was also studied. It was found that acids are powerful catalysts of the hydrolysis. The effect is most noticeable in media containing but little water, and diminishes as the proportion of the water increases, being least obvious in pure water. The value of the velocity factor is a linear function of the concentration of the acid. Alkalies and hydrolyzed salts were also found to act as strong catalysts of the hydrolysis in aque-

5 Zeit. physik. Chem. **67,** 501 (1909).
6 Journ. Chem. Soc. **97,** 733, 1677 (1910).
7 Journ. Chem. Soc. **101,** 1708 (1912).

ous solutions. The following equations were given to represent the mechanism of the hydrolysis:

$$\begin{array}{lll} \text{(I)} & Ac_2O \quad H_2O & = 2AcOH \\ \text{(II)} & Ac_2O + H_2O + H^+ & = 2AcOH + H^+ \\ \text{(III)} & Ac_2O + H_2O + HX & = 2AcOH + HX \\ \text{(IV)} & Ac_2O + H_2O + OH^- & = 2AcOH + OH^- \end{array}$$

Any one of the four forms could predominate according to the conditions, medium, etc. In aqueous solutions the choice lies between (I), (II), and (IV).

Philip[8] made a study of the reaction between acetic acid and water in glacial acetic acid and by determining the freezing-points of the mixture at frequent intervals.

Wilsdon and Sedgwick[9] studied the rate of hydrolysis of a number of acid anhydrides. The rate of formation of the acid was determined by measuring the increase in the electrical conductivity of a solution of the anhydride in water.

Verkade[10] also made use of the conductivity method. His results for the hydrolysis of acetic anhydrides agree very closely with those obtained by Rivett and Sidgwick.[6]

HYDROLYSIS OF SALTS.

It is a well-known fact that certain salts, even though they contain the strictly equivalent quantities of acid and base required for "neutrality," when dissolved in water are not neutral to indicators but react either acid or alkaline. This was first noticed by H. Rose[11] in working with certain basic salts, but was not explained satisfactorily until Arrhenius proposed his theory of electrolytic dissociation. In the light of this theory acidity is due to the presence of an excess of hydrogen ions, and alkalinity to the presence of an excess of hydroxyl ions. These ions cannot be accounted for by the salts themselves, therefore they must be accounted for by the water.

8 Proc. Chem. Soc., **28,** 259.
9 Journ. Chem. Soc., **103,** 1959 (1913).
10 Rec. Trav. Chim. **35,** 79 (1915).
11 Pogg. Ann. **83.** 132, 417 (1851).

Water must contain both hydrogen and hydroxyl ions. The ionization constant of water can be calculated by the equation—

$$\frac{H^+ \times OH^-}{H_2O} = k$$

Since the active mass of the nonionized water is so great in comparison with the active mass of the ions, it may be considered constant. We then have—

$$H^+ \times OH^- = k_{H_2O}$$

the value of k being 1.2×10^{-14} at 25°. This ionization is the same in all aqueous solutions. The value k_{H_2O} however, increases with rise in temperature. This increase is most probably due to the breaking down of the associated molecules into the simpler ones which are more easily dissociated. Pure water contains an equal number of hydrogen and hydroxyl ions, and therefore must react neutral. Furthermore, this relation holds for any neutral solution. To be acidic, a solution must contain an excess of hydrogen ions; to be basic, an excess of hydroxyl ions. To determine, then, whether a solution is neutral or not we make use of indicators, such as litmus, methyl orange, phenolphthalein, which give evidence by their color changes.

When a normal salt is dissolved in water partial hydrolysis takes place, yielding free acid and free base. Whether the solution will react acid or alkaline will depend on the degree of dissociation of these products of hydrolysis. It follows, therefore, that there are four types of salts which may undergo hydrolysis: (1) salts derived from strong acids and strong bases; (2) salts of weak acids and strong bases; (3) salts of strong acids and weak bases; (4) salts of weak acids and weak bases.

All salts except those of the first type are hydrolyzed to a considerable extent, due to the small degree of disso-

ciation of one or both of the products of hydrolysis. Salts of strong acids and strong bases under ordinary conditions do not undergo hydrolysis.

The determination of the degree of hydrolysis is not accomplished without difficulty. The free acid or base cannot be directly titrated with a standard solution, for equilibrium would be destroyed at once and neutrality would be reached only when the salt was completely decomposed. A method must then be employed which will not destroy the hydrolytic equilibrium. The methods most generally used are: (1) the determination of the velocity constant for the hydrolysis of an ester,[12] for this is proportional to the amount of free acid or alkali present; (2) the determination of the rate of inversion of cane sugar,[12]; (3) the determination of the electrical conductivity of the solution;[12] (4) the determination of the coefficient of distribution between two solvents.[12] In addition to these there are also many other methods of more or less limited applicability.

Only those salts were used in this investigation which were proved by the above methods to be nonhydrolyzed. For these salts the values of k calculated according to the equation—

$$\frac{(\text{Salt})}{(\text{Acid}) \times (\text{Base})} = \frac{k}{k_{H_2O}}$$

are so small that they need not be taken into account. The salts were further tested according to an observation made by Salm,[13] that salts which give no reaction with litmus have a concentration of H^+ and OH^- ions less than 1×10^{-6}, a value so small that it is negligible.

NEUTRAL SALT ACTION.

In a discussion of neutral salt action one must dis-

12 R. C. Farmer, B. A. Reports, 240 (1901).
13 Zeit. physik. Chem. **57**, 471 (1907).

tinguish clearly between the effect produced by a neutral salt on the catalytic activity of an acid (or alkali), and the effect of the neutral salt on hydrolysis by water alone. It is the latter effect in which we are most interested in this investigation, although the former is what is generally understood by the term "neutral salt action."

Effect of Neutral Salts on the Catalytic Activity of Acids.—It was clearly found[14] that the addition of a substance which is largely ionized in aqueous solution alters the rate of hydrolysis of esters or of carbohydrates by strong acids. This has been proved by the addition of metallic chlorides to mixtures in which hydrochloric acid is the catalyst, the addition of bromides to hydrobromic acid, and of nitrates to nitric acid. Those chlorides which are highly dissociated have much the same effect, while a salt like mercuric chloride which is only partially ionized has a much feebler action. Non-electrolytes such as the alcohols or sugars have but little effect on the hydrolytic activity of the hydrogen ions.

The action of the neutral salt is not always to accelerate the hydrolysis; often there is a retardation. There are also well-defined differences between the influence of neutral salts on the rate of inversion of cane sugar in the presence of acids and their influence in the catalytic hydrolysis of esters. The velocity of the inversion of cane sugar is increased to a much greater extent by the addition of certain concentrations of salts than is the velocity of the hydrolysis of esters.

Neutral salts have in general a retarding effect upon the hydrolysis of esters and amides by alkalies. Senter,[15] however, found that the hydrolysis of sodium chloroacetate by sodium hydroxide was greatly accelerated by the presence of neutral salts. It has been shown that neutral salt action is independent of the concentration of the compound hydrolyzed; is proportionally greater the more

14 Journ. prakt. Chem. **85,** 321, 401 (1862).
15 Journ. Chem. Soc. **91,** 473 (1907).

dilute the acid solution; is not greatly influenced by temperature or pressure; and is independent of the nature of the acid employed as catalyst.

In addition, Poma[16] has determined that the intensity of the action developed by neutral salts bears a strict relation to the chemical nature of the ions of the salts, and diminishes in passing from chlorides to bromides to nitrates to iodides, in succession; that it is independent of the chemical nature of the cations; and, finally, that it seems to be proportional not to the concentration of the salt in the solution, but to the concentration of the ions.

Effect of Neutral Salts on Hydrolysis by Water Alone.—Probably the first work done on neutral salt action in the absence of an acid was by Smith,[17] who investigated the effect of neutral salt on the rate of inversion of cane sugar. He found that salts of weak acids had almost no effect, while potassium chloride and sodium sulphate, the more nearly neutral salts, had considerable effect.

Senter showed that neutral salts have practically no effect on the decomposition of sodium chloroacetate by water.

Kellogg[18] studied the effect of the neutral salts, potassium chloride, potassium bromide and potassium iodide on the velocity of the hydrolysis of ethyl acetate. The reactions were carried out in sealed tubes at 100°, using a fixed quantity of ester and varying concentrations of the salt solution. The results obtained show that the specific influence of salts is greater in somewhat dilute solutions. As the concentration is increased, the effect gradually becomes less; until it reaches zero, and then becomes negative in character; for example, a 4-normal solution of potassium chloride hydrolyzes the ester more slowly than pure water itself. Kellogg found a decrease in the accelerating power from chloride to bromide to iodide, which is in reverse order to their stability.

16 Medd. K. Vetenskapsakad. Nobelinst. **2,** No. 11. pp. 1-28.
17 Zeit. physik. Chem. **25,** 144 (1898).
18 Journ. Amer. Chem. Soc. **31,** 403, 886 (1909).

Henderson and Kellogg[19] continued the investigation using the chlorides of sodium, lithium, calcium, strontium and barium, and the chloride and iodide of cadmium. They carried out the work under the same conditions as before, and in addition measured the conductivities and viscosities of the solutions at the concentrations and temperatures employed in the experiments, and from these calculated the degree of ionization. They found that the salts which produce the greatest effect are those which are the least ionized. The accelerating effect of lithium chloride is greater than that of sodium chloride although the degree of ionization of the former is less; while the chlorides of calcium, barium and strontium have a greater effect than either sodium chloride or potassium chloride, although they too are less ionized. Cadmium chloride, the least ionized of all the chlorides studied, produced the greatest effect, due probably to the hydrolysis of the salt. Henderson and Kellogg concluded that the effect produced by neutral salt on the hydrolysis of ethyl acetate is due to a specifice influence on the non-ionized portion of the salt, rather than to any function of the ions.

Holmes and Jones,[20] and later Lyons, Connolly and Jones, for reasons to be discussed later, took up the study of the influence of neutral salts on the rate of hydrolysis of methyl acetate and methyl formate by water. They used three concentrations of salt solutions: molar, half-molar and quarter-molar, and found that with a few exceptions all the salts studied have a pronounced accelerating effect upon the hydrolysis. They also found that there is a concentration of the neutral salt at which the effect is a maximum.

There have been several suggestions put forward to explain neutral salt action. Arrhenius[21] proposed that the salts may affect the substance which is being hydrolyzed;

19 Journ. Amer. Chem. Soc. **35,** 396 (1913).
20 Carnegie Inst. Wash. Pub. No. 230 (1915).
21 Zeit. physik. Chem. **4,** 226 (1889).

that there may be present in the solution an equilibrium between an active and an inactive form of the substrate, and that this equilibrium may be altered through changes of temperature or ionic concentration. Armstrong and Caldwell concluded that the salts act by removing part of the water in the form of definite hydrated compounds, and in this manner increase the concentration of the reacting substance. Stieglitz explained salt effect in general by the theory that the presence of salts in the solution increases the dielectric constant, or, at any rate, the ionizing power of the solvent. All of these theories are plausible, but it is highly improbable that neutral salt action is due to any one cause exclusively.

STATEMENT OF THE PROBLEM.

Anderson and Jones[22] found that the absorption spectra of solutions of salts like neodymium chloride and nitrate, in non-absorbing solvents like water and alcohol, depend largely on the nature of the solvent in which the salt was dissolved; for example, neodymium chloride dissolved in water has a different spectrum from that of neodymium chloride dissolved in methyl or ethyl alcohol. They found for the first time what they called "solvent bands," showing that the dissolved substance was combined with more or less of the solvent forming in the one case "hydrates" and in the other "alcoholates." Alcoholates had, as would be expected, very different resonance from hydrates.

Strong and Jones[23] extended the work of Anderson and Jones to a large number of solvents and to a fairly large number of non-absorbing salts, and showed that these solvents had a marked influence on the absorption spectra of the salts dissolved in them. They were able to dis-

22 Carnegie Inst. Wash. Pub. No. 110 (1909).
23 Carnegie Inst. Wash. Pub. No. 130 (1910); No. 160 (1911).

tinguish between the spectra of salts dissolved in a normal alcohol and those in the isomeric alcohol.

Guy and Jones[24] built the most sensitive radiomicrometer constructed up to that time, and by means of it they studied quantitatively the intensities of absorption lines and bands. They found that while solutions of slightly hydrated salts were about equally transparent with pure water, solutions of strongly hydrated salts were very much more transparent than pure water.

The work of Guy and Jones was repeated by Shaeffer, Paulus and Jones,[25] using an even more sensitive radiomicrometer constructed by Shaeffer; and they confirmed the conclusions reached by Guy and Jones. They found solutions of strongly hydrated salts which were as much as 40 per cent. more transparent than a depth of pure water equal to the water in the solution in question. This showed that water of hydration has a very different resonance from pure water.

Having found this physical difference between combined and free water, the problem was then to see if there was any chemical difference. Therefore, Holmes and Jones[20] took up a study of the action of strongly hydrated salts and slightly hydrated salts on the hydrolysis of methyl acetate and methyl formate. The method used consisted in measuring the velocity of hydrolysis of the ester by pure water and by solutions of slightly and strongly hydrated salts. The solutions were prepared in such a way that the amount of water in each was the same, and was equal to the amount of pure water employed. Taking into account the hydrolysis of the strongly hydrated salts, they found that these salts hydrolyzed the ester much more rapidly than pure water itself.

The reaction studied by Holmes and Jones was a very slow one and indicated that combined water has greater

24 Carnegie Inst. Wash. Pub. No. 190 (1913).
25 Carnegie Inst. Wash. Pub. No. 210 (1915).

activity than free water. We wished to investigate the same problem, using a reaction that proceeded much more rapidly; therefore we chose the reaction involving the conversion of acetic anhydride into acetic acid.

EXPERIMENTAL.

Purification of Acetic Anhydride.

Pure acetic anhydride was necessary for the work. The physical properties as described in the literature vary greatly. The boiling-points given range anywhere from 135°-140°, at 760 mm. pressure. The densities given vary between 1.07 and 1.09. From this it can be seen that it was impossible to test its purity by the ordinary simple means. Acetic acid is the impurity most likely to be present in the anhydride, and is very difficult to detect if only small amounts are present. 0.51 gram of pure acetic anhydride, when completely hydrolyzed, is equivalent to 100 cc. N/10 solution of sodium hydroxide; while the same weight of mixture containing 1 per cent. of acetic acid is equivalent to 99.85 cc. This is within the experimental error.

Methods of finding the actual percentage of acetic acid and anhydride in a mixture have been given by Pickering,[26] Menschutkin and Vasilieff,[27] Treadwell,[28], Edwards and Orton,[29] and Orton and Jones.[30] Pickering determined the freezing-points of the solutions of anhydride and water, and compared them with the freezing-points of known concentrations of acetic acid. Menschutkin

26 Journ. Chem. Soc. **63,** 1000 (1893).
27 Journ. Russ. Phys. Chem. Soc. **21,** 190 (1889).
28 Analytical Chemistry, 1914, Volume II.
29 Journ. Chem. Soc. **99,** 1181 (1911).
30 Journ. Chem. Soc. **101,** 1720 (1912).

and Vasilieff treat with aniline and water, and determine the acidity after the reaction—

$$C_6H_5NH_2 + (CH_3CO)_2O = C_6H_5NHCOCH_3 + CH_3COOH$$

has taken place. Treadwell recommends treatment with barium hydroxide solution and titration of the excess of the latter; while Edwards and Orton convert the anhydride into acetanilide, the latter into phenylacetylchloramine, and then determine the chloramine volumetrically.

The method finally adopted to purify the acetic anhydride was that of repeated distillation, using a five-bulb distilling head and discarding the first and last fractions. This gave an anhydride which distilled practically constant at 138°-139°. Specific gravity determinations, using a 10 cc. pycnometer, gave a mean value of 1.0852 at 15°/4°. The acetic anhydride was further tested by titrating weighed samples directly, and by titrating weighed samples using the method advocated by Menschutkin and Vasilieff.

PURIFICATION OF SALTS.

Only the purest salts obtainable were used. They were usually Kahlbaum preparations, although some of other well-known firms were used.

These salts were dissolved in conductivity water, filtered from any foreign matter present, and then recrystallized one or more times.

APPARATUS.

Thermostats.—The constant-temperature baths were of the improved form designated by Davis[31] of this laboratory. These baths are substantially constructed of copper and are of about 60 liters capacity. Gas is used

31 Carnegie Inst. Wash. Pub. No. 210 (1914).

for maintaining constant temperature, the heat being applied directly to a heavy galvanized iron pipe outside the bath, through which a part of the water is kept circulating by means of the propellers. Only a small portion of the water in the thermostat comes into immediate contact with the heated surface, and this portion is subsequently mixed with the main body of water, thereby securing much more even distribution of temperature. In these baths the temperature can be kept constant well within 0.02°.

The thermometers were of the differential Beckman type. They were compared with a standard thermometer, which had been calibrated at the Bureau of Standards.

Flasks, pipettes and burettes for measuring purposes were all carefully calibrated by weight.

All bottles used (varying in content from 50 cc. to 6 l.), and all measuring flasks were of Jena glass.

A special apparatus was used for the alkali solution, to protect it from carbon dioxide and water vapor in the air.

SOLUTIONS.

The water used in the preparation of the solutions was purified by the method of Jones and Mackay[32] as modified by Schmidt.[33] It had a conductivity at no time greater than 2×10^{-6}.

The aniline used to combine with the excess of acetic anhydride was the purest obtainable. It was further distilled as many times as necessary to remove all decomposition products. The slightly colored product was then kept in a cupboard protected from light.

The solutions of the non-hydrated salts were made up directly by weight, while those of the hydrated salts were analyzed gravimetrically and diluted to the required

32 Amer. Chem. Journ. **17,** 83 (1895).
33 Amer. Chem. Journ. **19,** 90 (1897).

strengths. The chlorides of barium, strontium, calcium and magnesium were determined as silver chloride, and the sulphates of sodium and magnesium were determined as barium sulphate.

The solution of sodium hydroxide used in titrating the acetic acid formed by the hydrolysis of the acetic anhydride was made up approximately half-normal, using "sodium hydroxide from alcohol." It was preserved in an apparatus protected from the impurities in the air. It was standardized by titration against a solution of sulphuric acid of about the same strength (0.4115 N.) The sulphuric acid had been standardized as barium sulphate.

The indicator used was phenolphthalein, as it gives the best results in titrating a weak acid with a strong alkali; the only objection being that it is also sensitive to carbonic acid. Corallin had been tried, but was not so satisfactory.

METHOD OF PROCEDURE.

The method in principle is a modification of that of Menschutkin and Vasilieff,[1] and later employed by A. and L. Lumiere and Barbier[3],[4]. In order that the results should be comparable, the amount of water present must be kept constant, therefore the specific gravity of the salt solution was first taken, giving the weight of 1 cc. From analysis that part of the weight due to the anhydrous salt alone was known for each cubic centimeter. This known weight of salt, subtracted from the weight of 1 cc. of solution, gave the weight due to the pure water alone. This, divided into the weight of 1 cc. of pure water at that temperature, gave the amount of solution in cubic centimeters equivalent to 1 cc. of pure water. The amount of solution thus calculated was pipetted into a 250 cc. Jena bottle. An equivalent of 100 cc. of pure water was taken in all determinations. The bottle was suspended in the con-

stant temperature bath. There was also placed in the bath a bottle containing the anhydride and a number of small empty bottles of 50 cc. capacity.

When all had come to the temperature of the bath, the bottle was removed and 5 cc. of the anhydride introduced. Time was reckoned from when the anhydride was first added. Solution took place immediately on shaking except in the case of the very concentrated solutions. Equal aliquot portions were removed and placed in the small 50 cc. bottles, the whole being kept in the bath. These small bottles were removed, first every 5, then every 10 minutes, and a slight known excess of aniline added. On shaking, this combines with the residual acetic anhydride, precipitating acetanilide and liberating an equivalent of acetic acid. In one bottle of each series the reaction was allowed to go to completion without the addition of aniline, so as to control the results obtained.

The total amount of acetic acid was then determined in the bottle by titration with the half-normal solution of sodium hydroxide in the presence of phenolphthalein as indicator. Never less than 10 cc. nor more than 25 cc. of alkali, as measured in a 50 cc. burette, was required to neutralize the acetic acid.

Two temperatures, 15° and 25°, were employed. Only one concentration of acetic anhydride was used (approximately 5 per cent.), because if two were employed the results would not be comparable on account of volume changes. For the salts molar, half-molar and quarter-molar solutions were taken in all cases and whenever possible solutions of greater concentration.

Measurements of the velocity were not taken for longer than 60 minutes at 15° and 40 minutes at 25°, for it was found that the hydrolysis of the acetic anhydride by water was then practically complete.

CALCULATION.

From the total amount of acetic acid, as determined by titration with the alkali, that due to the water alone must be calculated. The simple formula—

$$y = 2z - x$$

is used, where y is the amount of acetic acid due to the water alone, z is the total amount of acetic acid measured by titration, and x is the total amount of acid that can be formed if all the acetic anhydride has been hydrolyzed.

The results obtained for the "control" bottles, when substituted in the formula, should give the same values for x and y, which would be equivalent to 100 per cent. hydrolysis.

DATA.

In the following tables the concentrations of salt solutions are M, molar; M/2, half-molar, etc. Time is expressed in minutes. All results are expressed in percentages, 100 per cent. meaning complete hydrolysis of the acetic anhydride. In each table there is placed for comparison a column showing the percentage decomposition of acetic anhydride by water alone.

TABLE I.

Potassium Chloride at 15°.

	Concentration.					
Time	Water	3 M	2 M	M	M/2	M/4
5	30.99	14.68	21.71	26.79	29.2	31.28
10	54.15	30.16	38.96	48.85	50.07	53.55
20	78.43	49.67	59.93	69.72	73.51	77.33
30	90.22	63.67	73.57	82.70	86.53	89.16
40	96.87	73.70	83.09	90.76	93.21	94.32
50	98.18	81.65	89.24	94.51	96.61	97.48
60	99.01	86.54	92.36	97.08	98.13	98.63

TABLE II.

Potassium Chloride at 25°.

Concentration.

Time	Water	3 M	2 M	M	M/2	M/4
5	44.54	24.82	27.58	36.56	42.18	44.14
10	72.76	45.68	55.12	64.98	68.88	71.98
20	93.71	70.82	84.63	87.87	91.08	92.16
30	98.31	84.63	91.50	95.99	96.99	97.59
40	99.53	91.86	94.81	98.13	98.64	99.00

TABLE III.

Sodium Chloride at 15°.

Concentration.

Time	Water	4 M	3 M	2 M	M	M/2	M/4
5	30.99	19.24	21.37	24.84	30.44	32.21	33.71
10	54.15	24.49	33.64	42.71	52.79	54.87	55.98
20	78.43	40.87	54.07	65.04	75.14	77.88	79.38
30	90.22	56.04	67.90	79.43	87.42	89.09	89.42
40	96.87	64.75	77.06	86.47	92.12	94.20	94.65
50	98.18	73.23	84.53	90.95	97.13	97.70	97.99
60	99.01	79.02	88.78	94.08	98.21	98.53	98.73

TABLE IV.

Sodium Chloride at 25°.

Concentration.

Time	Water	4 M	3 M	2 M	M	M/2	M/4
5	44.54	21.80	28.93	35.44	42.23	44.65	46.91
10	72.76	36.85	50.48	60.97	60.07	72.53	73.87
20	93.71	60.09	75.62	84.93	90.30	91.90	93.51
30	98.31	75.73	87.85	93.45	97.56	97.95	98.57
40	99.53	85.90	93.91	97.28	98.75	99.26	99.69

TABLE V.

Calcium Chloride at 15°.

Concentration.

Time	Water	4 M	M	M/2	M/4
5	30.99	2.80	33.98	34.34	34.01
10	54.15	15.60	55.67	56.48	56.58
20	78.43	41.37	80.86	81.08	81.19
30	90.22	57.97	90.45	91.87	92.04
40	96.87	69.51	95.72	96.20	96.96
50	98.18	77.85	97.49	99.13	98.25
60	99.01	83.95	98.90	99.84	99.19

TABLE VI.

Calcium Chloride at 25°.

Concentration.

Time	Water	4 M	M	M/2	M/4
5	44.54	20.18	48.36	48.61	48.79
10	72.76	49.93	75.24	76.23	76.81
20	93.71	78.20	93.76	94.52	94.56
30	98.31	92.23	99.81	97.94	97.51
40	99.53	96.16	100.00	99.37	99.65

TABLE VII.

Magnesium Chloride at 15°.

Concentration.

Time	Water	4 M	2 M	M	M/2	M/4
5	30.99	1.30	20.37	30.01	30.49	32.95
10	54.15	14.15	37.30	49.83	51.71	54.64
20	78.43	24.80	58.84	73.29	75.81	78.32
30	90.22	52.32	73.62	85.01	88.17	89.93
40	96.87	70.00	82.22	92.15	93.74	95.09
50	98.18	86.61	88.35	94.62	96.96	97.43
60	99.01	89.73	92.09	97.76	98.73	99.31

TABLE VIII.

Magnesium Chloride at 25°.

Concentration.

Time	Water	4 M	2 M	M	M/2	M/4
5	44.54	1.80	29.52	40.01	41.60	43.09
10	72.76	25.36	56.29	69.41	70.89	72.08
20	93.71	73.30	79.97	89.79	92.39	93.31
30	98.31	92.54	91.74	96.16	97.07	97.89
40	99.53	96.73	97.15	98.45	98.84	99.08

TABLE IX.

Barium Chloride at 15°.

Concentration.

Time	Water	M	M/2	M/4
5	30.99	30.51	31.49	34.48
10	54.15	50.56	54.98	56.88
20	78.43	74.68	78.60	81.05
30	90.22	86.83	90.30	91.09
40	96.87	92.96	95.76	96.20
50	98.18	97.09	97.66	98.10
60	99.01	98.10	99.10	99.88

TABLE X.

Barium Chloride at 25°.

Concentration.

Time	Water	M	M/2	M/4
5	44.54	39.57	42.04	46.89
10	72.76	68.43	73.23	75.90
20	93.71	91.25	92.00	93.94
30	98.31	97.85	97.99	98.19
40	99.53	98.44	98.72	98.85

TABLE XI.

Strontium Chloride at 15°.

Concentration.

Time	Water	2 M	M	M/2	M/4
5	30.99	20.80	27.44	32.33	35.22
10	54.15	39.43	48.17	55.15	57.00
20	78.43	63.31	74.88	78.86	80.89
30	90.22	76.46	87.19	90.56	92.07
40	96.87	84.93	94.40	95.89	96.30
50	98.18	89.84	97.28	98.00	98.43
60	99.01	92.18	98.42	99.08	99.32

TABLE XII.

Strontium Chloride at 25°.

Concentration.

Time	Water	2 M	M	M/2	M/4
5	44.54	31.40	41.11	47.17	47.89
10	72.76	57.58	72.15	74.35	76.01
20	93.71	84.43	90.86	92.87	94.37
30	98.31	94.38	96.47	98.79	98.85
40	99.53	98.19	98.71	99.58	99.64

TABLE XIII.

Sodium Sulphate at 15°.

Concentration.

Time	Water	M	M/2	M/4
5	30.99		38.98	37.16
10	54.15		65.30	60.57
20	78.43		86.15	83.74
30	90.22		94.07	93.27
40	96.87		96.64	96.43
50	98.18		98.32	98.13
60	99.01		99.65	98.97

TABLE XIV.

Sodium Sulphate at 25°.

Concentration.

Time	Water	M	M/2	M/4
5	44.54	61.51	54.62	50.52
10	72.76	87.56	82.84	79.32
20	93.71	98.16	96.95	96.02
30	98.31	99.38	99.22	99.16
40	99.53	99.83	99.71	99.63

TABLE XV.

Magnesium Sulphate at 15°.

Concentration.

Time	Water	M	M/2	M/4
5	30.99	41.62	41.88	37.99
10	54.15	66.49	67.34	61.09
20	78.43	86.65	88.45	83.71
30	90.22	92.71	96.43	93.33
40	96.87	94.85	98.30	96.96
50	98.18	97.44	98.83	98.96
60	99.01	98.37	99.13	99.43

TABLE XVI.

Magnesium Sulphate at 25°.

Concentration.

Time	Water	M	M/2	M/4
5	44.54	56.61	50.98	55.23
10	72.76	84.26	78.72	80.46
20	93.71	95.49	95.82	95.99
30	98.31	96.48	98.17	98.29
40	99.53	98.13	99.71	99.82

TABLE XVII.

Potassium Nitrate at 15°.

Concentration.

Time	Water	2 M	M	M/2	M/4
5	30.99	21.93	26.50	30.59	31.78
10	54.15	36.35	44.79	51.24	53.35
20	78.43	58.29	64.15	74.33	77.15
30	90.22	71.53	80.91	86.18	88.76
40	96.87	81.37	87.11	92.74	94.85
50	98.18	89.93	93.80	95.91	97.20
60	99.01	92.27	96.14	97.43	98.49

TABLE XVIII.

Potassium Nitrate at 25°.

Concentration.

Time	Water	2 M	M	M/2	M/4
5	44.54	34.44	35.56	37.03	41.64
10	72.76	51.90	54.37	65.93	69.71
20	93.71	77.03	82.07	88.45	90.92
30	98.31	88.69	94.58	96.48	98.01
40	99.53	94.94	97.30	98.60	98.84

TABLE XIX.

Sodium Nitrate at 15°.

Concentration.

Time	Water	2 M	M	M/2	M/4
5	30.99	21.69	26.38	32.36	33.66
10	54.15	36.23	45.73	53.12	54.52
20	78.43	59.80	70.35	77.27	79.14
30	90.22	73.51	81.95	87.93	89.11
40	96.87	81.49	91.10	93.61	94.85
50	98.18	89.11	94.38	97.81	96.85
60	99.01	92.47	97.01	98.07	98.37

TABLE XX.

Sodium Nitrate at 25°.

Time	Concentration. Water	2 M	M	M/2	M/4
5	44.54	33.14	36.80	41.07	41.64
10	72.76	54.72	63.93	69.01	69.94
20	93.71	80.20	86.68	90.58	90.92
30	98.31	91.87	95.77	97.06	97.54
40	99.53	96.59	97.89	98.24	98.83

DISCUSSION.

There is one difficulty in the study of this problem that must first be pointed out, i. e., the use of a strong alkali solution (half-normal NaOH) with which to titrate the acetic acid formed. This necessarily introduces some error, since a difference of 0.1 cc. in reading the burette would make a difference of over 1 per cent. A more dilute solution of alkali could not be used since too large a quantity of such a solution would be required.

The rate of decomposition of the acetic anhydride is at first very rapid, being almost complete at 25° in 5 minutes and nearly three-quarters complete at the end of 10 minutes, then gradually decreasing as the reaction approaches completion. In this respect the reaction differs from similar ones studied, such as the hydrolysis of esters, since in these cases the reactions are reversible. Temperature has a marked accelerating influence on the hydrolysis, the velocity of the reaction as a whole, and the increase for succeeding intervals of time, being much greater at 25° than at 15°.

All the salts studied, with the exception of sodium sulphate and perhaps also magnesium sulphate, have in the case of the greater concentrations a retarding influence

on the hydrolysis. This retardation diminishes as the salt solution becomes more and more dilute. With sodium sulphate solutions the reverse is true, the more concentrated the solution the greater is the accelerating effect. This is also true to a certain extent with magnesium sulphate, although the effect is not as pronounced.

In the case of both magnesium salts studied, magnesium chloride and magnesium sulphate, it was difficult to get clear, clean-cut results. In titrating the acetic acid with the alkali in the presence of these salts a good end-point could not be reached. The color of the indicator, phenolphthalein, appeared to be masked, especially in the more concentrated solutions.

All the non-hydrated salts studied have an hindering effect on the hydrolysis. The amount of this hindrance under the same conditions is practically the same for the four salts studied, there being at no time a variance of more than a few per cent. With the most dilute solutions studied, quarter-molar, the results for the decomposition are practically the same as for pure water.

The hydrated salts, with the exception of magnesium chloride, all give results for the decomposition greater than those of the non-hydrated ones, while with the more dilute solutions there is an appreciable acceleration of the hydrolysis of the acetic anhydride over that due to pure water alone. Sodium sulphate and magnesium sulphate at all concentrations studied have a very marked accelerating effect on the hydrolysis. Greater concentrations of these salts were not used for the reason that they do not mix with the anhydride at once on simple shaking. Calcium chloride, strontium chloride and barium chloride also have an accelerating influence on the hydrolysis in the more dilute solution. Magnesium chloride acts as do the non-hydrated salts, having a retarding influence at all dilutions.

BIOGRAPHY.

Gerald Charles Connolly was born near Pikesville, Baltimore County, Maryland, on August 7, 1890. He received his early education in the public schools of Baltimore and received his A.B. degree from Rock Hill College (Maryland). He then entered The Johns Hopkins University as a graduate student in Chemistry taking as his subordinates Physical Chemistry and Physics. He received during the years 1914-15 and 1915-16 university scholarships.